



Comparison of Physicochemical Properties of Edible Libyan Olive Oils and other international Olive Oils

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ABSTRACT

The purpose of this study was to evaluate the physicochemical characteristics of olive oils. The samples collected from three different olive from Benghazi city. In addition, Tunisian and Italian olive oil samples were used as compared samples. The Moisture, %FFA, acid value, saponification number, ester value, peroxide values, and their applicability as edible oils were examined. Based on our results the physio-chemical characteristics of olive oils from Benghazi presses have a significantly high acid value of 19.98 and 10.97 besides, % FFA was ranged from 5.527 to 10.064% of oleic acid for sample No. 3 and sample No. 1 respectively, and the B₃ sample has a maximum moisture content of 0.47% m/m and the minimum content of moisture 0.0882% m/m for Italian sample. Meanwhile, the ester values varied between 164.89 to 194.53 mg KOH/g, and the peroxide values ranged between 0.527 to 0.784 Meq O₂/kg and have a saponification value from 184.884 to 195.922. The concluded results were in agreement with the International Olive Oil Council's (IOOC) permissible ranges, with exception for the acid value and free fatty acid percentage in olive oil presses from Benghazi city.

Keywords: Physicochemical; Acid value; Ester values; Saponification; Peroxide value.

1. Introduction

Olive oil is one of the oldest vegetable oils mainly produced in countries around the Mediterranean Sea. It is a natural fruit juice; its consumption is increasing throughout the world due to its nutritional and pleasant flavor, which has an increase in consumption. The fruit of the *Olea europaea* L. tree,

which is a member of the olive family and is native to the Mediterranean region, is used to make olive oil through mechanical extraction. [1,2]

The importance of olive oil is related to its high levels of monounsaturated fatty acids (mainly oleic acid), and several antioxidants. Oil with higher

monounsaturated fatty acids (MUFAs) and lower saturated fatty acids (SFAs) are preferred because of the proven beneficial effect of MUFAs on serum cholesterol levels. [3]

Olive oils possess numerous nutritional benefits which are primarily related to the fatty acid composition, mainly due to both the high content of oleic acid and the balanced ratio of saturated and polyunsaturated fatty acids. Olive oil is rich in monounsaturated fatty acids and low in saturated fatty acids. In addition, olive oil contains considerable amounts of natural antioxidants and is considered important in the prevention of many diseases. [4] Also there is a lot of evidence that refers to the biological activity of Olive oil consumption in reducing neuron diseases, Alzheimer's, cancer, and diabetes. [5]

International Olive Council (IOC, 2006) and the European Commission (EEC, 1991) have defined the quality of olive oil based on parameters that include free acidity, peroxide value (PV). In particular, the quantity of free acidity is an important factor for classifying olive oil. [6]

This study was concerned with assessing the quality and purity parameters of olive oil samples from different sources according to regulations of CODEX STAN 33-1981(FAO & WHO), based on parameters that include physicochemical properties like percent of moisture content, specific relative density, acid value, peroxide value, saponification value, and ester value.

2. Materials and Methods

2.1. Materials

Olive oil samples were collected from three different olive presses from Benghazi city and represented as B₁, B₂, and B₃. The samples of olive oil were packaged in sterilized polypropylene (PP) bottles and kept in a dark room. Moreover, two olive oil samples were purchased from the local supermarket Tunisean (T) and Italian (I) samples which has referred to them as T and I and represent (Tunisia Pomace olive oil) and (Italian virgin olive oil) respectively.

2.2. Methodes

2.2.1. Determination of moisture content

Moisture content was determined by the weight of 20 g of the sample and placed in a pre-dried crucible that had already determined its blank weight (equation 1). The sample was heated at 105 °C for 1 hour until the cessation

of rising bubbles of steam and incipient smoking. Heated samples were cooled to room temperature in a desiccator and re-weighed, then weighted again the moisture content was calculated by difference. [7]

$$\text{Moisture content} = \frac{W-d}{W} \times 100\% \dots\dots\dots(1)$$

2.2.2. Determination of saponification value

Weight about 2 g of oil sample into a 250 ml Erlenmeyer flask. Then pipette 25 ml of the alcoholic potassium hydroxide solution into the flask. The resulting mixture was refluxed for 30 minutes, followed by addition of 3 drops of phenolphthalein indicator, and titrated with 0.5 M HCl until the color disappeared. This procedure was repeated without the oil and the calculated value determined from the blank value (equation 2). [8]

$$\text{Saponification value} = \frac{(\text{ml of HCl blank} - \text{ml of HCl Sample}) \times 56.1 \times N}{\text{Wt of sample (g)}} \dots\dots\dots(2)$$

2.2.3. Determination of acid value and % of free fatty acid

Taking approximately 2g of oil sample in a dried conical flask, then add 25ml of absolute ethanol, boiled it and 2-3 drops of phenolphthalein indicator were added into the mixture, that shaken in water bath at about 65 °C for 15minutes, after that the mixture was cooled and was titrated against 0.1N KOH solution. The acid value (AV) and free fatty acid (FFA) were calculated from the equations below. [9]

$$\text{Acid value (AV)} = \frac{\text{Vol. of KOH(ml)} \times N \text{ of KOH} \times 56.1}{\text{Wt of oil used(g)}} \dots\dots\dots(3)$$

$$\% \text{ Free fatty acid} = \frac{\text{Vol. KOH(ml)} \times N \text{ of KOH} \times M.Wt}{\text{Wt of oil used(g)} \times 10} \dots\dots\dots(4)$$

M.Wt = Molecular weight of the free fatty acid as Oleic acid [C₁₈H₃₄O₂=282.47g/mol]

2.2.4. Determination of ester value

Ester value, which is defined as the number of milligrams of potassium hydroxide required to saponify the fatty acid esters in one gram of the oil, was also determined for the oil extracted in this work. It was obtained as the difference between the saponification value and the acid value of the oil. [10]

Ester value = Saponification value – Acid value

2.2.5. Determination of peroxide value

Weight 1.0 g of oil sample in a flask, then add powdered potassium iodide 1.0 g and solvent mixture (2:1 glacial acetic acid:chloroform). The resulting solution was then placed on a water bath to dissolve property and then add 20ml of 5% potassium iodide. The sample solution was then titrated with 0.002N sodium thiosulphate using starch as indicator. [8]

$$PV = \frac{N \text{ of Na}_2\text{S}_2\text{O}_3 \times \text{vol. of Na}_2\text{S}_2\text{O}_3 \text{ consumed} \times 1000}{\text{Wt. of sample (g)}} \dots \dots (5)$$

3. Results and Discussion

Moisture content is an important determinant of oil quality and confirmatory check on the dryness of the oil sample. According to codex Stan 33-1981, an olive oil sample has a maximum moisture content of 0.1% m/m.[11] The fundamental for the estimation of the moisture content is the weight loss of the sample at the end of drying, high moisture content promotes hydrolytic rancidity of fats and oils, so It is desirable to keep the moisture content low as it will increase the shelf life by preventing oxidation and rancidity processes.[12] Considering the results obtained, the mean moisture content of collected samples ranged from 0.088 to 0.47%.

The high value of moisture content recorded for the B₃ sample outside the range of reference value of olive oil moisture content standard due to decreased quality of oil which may be related to water adulteration. On the other hand, the moisture content of (B₁ and B₂) samples tends to deviate a little from the standard value which found to be 0.2268 and 0.1813% respectively, at the

same time (T and I) samples tend to be within the standard range (0.1031- 0.0882%) respectively as illustrated in the (Table 1 and figure 1).

Saponification value (SV) is an estimate of oxidation during storage and is also an indication of the degree of decomposition of the oils. It is also used to calculate the fat or oil saponification number, it is a very important factor in soap production, which is an index of the triacylglyceride's average molecular weight in the sample. [13,14]

The saponification value represents the number of milligrams of potassium hydroxide required to saponify (1g) of fat under the conditions specified to measure the average molecular weight of all the fatty acids presented in this process. The high saponification value is due to its high concentration of short and medium-chain triglycerides. In contrast, saponification value for oils that contain a long chain of fatty acids is low due to fewer carboxylic groups for each mass unit of the oil when compared to short-chain fatty acids. [15,16]

Although, adulteration of fat or oil with unsaponifiable matter can lead to dropping in saponification value.⁹ The present results showed that the saponification number of olive oil samples ranged from 184 mg KOH/g in the B₃ sample to nearly 196 mg KOH/g in the B₂ sample, as shown in (Table 1 and figure 2), so the results were considered to be within the allowable range of the CODEX standard (184-196 mg KOH/g).

Table 1. Physicochemical parametera of olive oil presses from Benghazi city B₁, B₂, B₃ and from the local supermarket olive oil Tunisean (T) and Italian (I)

Code of sample Parameters	B ₁	B ₂	B ₃	T	I
Moisture content (% m/m)	0.226±0.021	0.181±0.032	0.470±0.048	0.103±0.014	0.088±0.01
Saponification value (mg KOH/g oil)	190.33± 1.34	195.92± 1.20	184.88± 1.291	195.37± 1.523	195.06± 1.34
% free fatty acid	5.53±0.067	0.928±0.087	10.06±0.836	0.328±0.082	0.279±0.01
Acid value (AV)	10.97±0.135	1.84±0.172	19.98±0.326	0.744±0.163	0.544±0.022
Ester value	180.29±3.368	194.09±2.227	164.89±4.569	193.55±1.678	194.53±1.32
Peroxide value (Meq active O ₂ /kg)	0.589±0.076	0.784±0.060	0.595±0.051	0.527±0.112	0.587±0.31

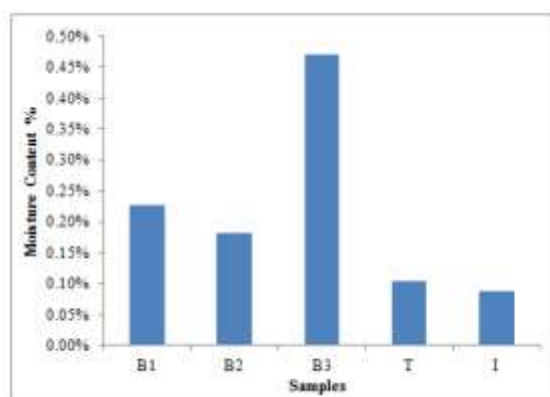


Fig. 1. % of moisture content of olive oil presses

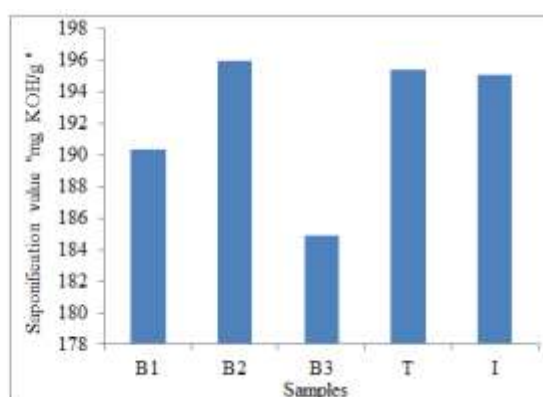


Fig. 2. saponification value of olive oil presses

Hydrolysis of fatty acids and glycerol from oils is important in the quality control of vegetable oils which indicate the extent of triglyceride hydrolysis so that free fatty acids are very low in high-grade lipid samples, which have been studied by determining the percentage of free fatty acids (%FFA) which is expressed as % of oleic acid (mass/mass). In the case of fatty acids, the acid value may be used in conjunction with the saponification value to measure the amount of neutral fat present.[9] Olive oil that is suitable for human consumption has a free acidity, expressed as oleic acid, of not more than 1 gram per 100 grams. CODEX 2013. The results obtained in the analysis showed that samples (B₁, B₃) with FFA values of 5.527% and 10.064 % respectively, which is significantly higher than the

permissible limit for free acidity given in the CODEX standard (1% of oleic acid), which may be related to the lipolytic action of the olive lipases themselves and/or the lipolytic enzymes produced by microorganisms living on olives, and compared to the results obtained for the samples collected (B₂, T, and I) the samples were within allowable limits (0.928, 0.328 and 0.279 %) respectively as shown in (table 1 and figure 3).

Acid value (AV) is analytically used to detect the level of unesterified fatty acid in a lipid sample to define its quality. The AV is used to assess the amount of oil that will be lost through the refining process designed to remove fatty acid. Hence, a high acidity level means a poorly refined oil or fat breakdown after storage or use.

[9,17] As a result, the AV values for samples (I, T, and B₂) were 0.544, 0.744, and 1.844 mg KOH/g of oil, respectively. As expected, the highest

values of acidity recorded for samples B₁ at 10.97 mg KOH/g of oil, and B₃ at 19.98 mg KOH/g. Both results

go along with the results obtained from the percent of FFA analysis as previously reported in (Table 1 and figure 4). Which represent indicate respective high levels of long-chain carboxylic acids in olive oil samples.

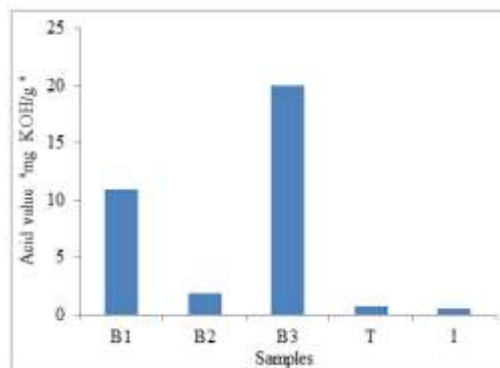


Fig. 3. Acid value of olive oil presses

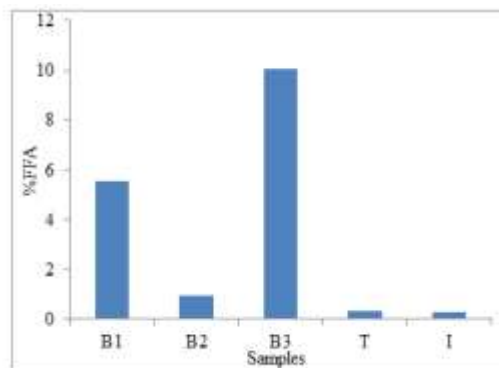


Fig. 4. % free fatty acid of olive oil presses

Ester value is the number of milligrams of potassium hydroxide required to hydrolyze the esters present in one gram of oil sample. This is the difference between saponification value and acid value. A high ester value indicates the presence of a high amount of ester and low molecular weight fatty acid content.[10] consequently, when the saponification number increases, the ester number will increase as well. According to our data which have been included in (Table 1 and figure 5) the same sample that has the lowest value of saponification 184.884 mgKOH/g has the lowest ester value 164.89 mg KOH/g.

The peroxide value of oil is an important property for measuring the degree to which rancidity is produced due

to autooxidation reactions that occurred during oil storage.[10] Peroxide value is a common method used to measure lipid oxidation and is suitable for measuring the formation of peroxide in the early stages of oxidation. unsaturated fatty acids react easily with oxygen to form peroxides.[18] It is clear that the peroxide value of all olive oil samples was below the value of 20 meq O₂/kg of olive oil, which is the maximum established by the Council for International Olive Oil, which may be related to natural antioxidants in olive oil, which lowered the oxidation process. (table 1 and figure 5), shows peroxide values where peroxide values ranged from 0.527 to 0.784 in the samples collected.

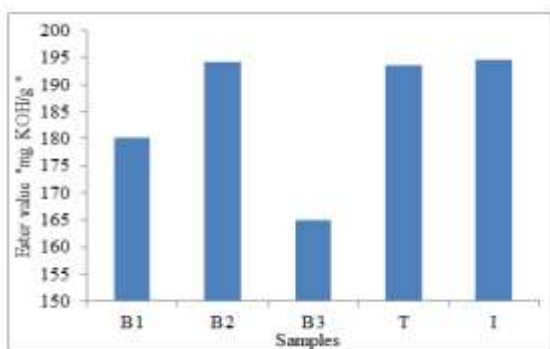


Fig. 5. Ester value of olive oil presses

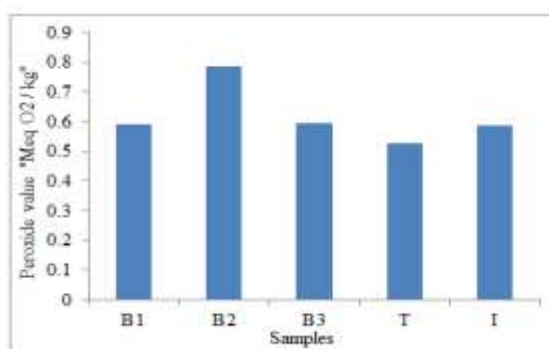


Fig. 6. Peroxide value of olive oil presses

4. Conclusion

The obtained results revealed that the Libyan Olive B oil samples exhibited remarkable physical and chemical properties and which are found to be within the permissible ranges of the International Olive Oil Council (IOOC) with exception of AV and %FFA for the B₁ and B₃ samples.

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